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Polarisation of the Lines in Raman Spectra.

By

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(Plate V.)

Abstract.

A systematic study is made of the state of polarisation of the various Raman lines occurring in some simple compounds, *viz.*, SO_2, CS_2, SO_3, NH_3, $CHCl_3$, $CHBr_3$, trichlorides of phosphorous, arsenic and bismuth and the tetrachlorides of carbon, silicon, titanium and tin. Close similarities are shown to exist between the polarisation characters of the Raman spectra arising from compounds having analogous structures. It is suggested that the geometry of the various oscillations is one of the chief factors which influence the polarisation of a Raman line. The depolarisation factor generally ranges from 0 to 1. Contrary to this however, in the case of SO_3, a Raman line shifted by 1403 wave numbers is found to have a depolarisation greater than unity. The significance of this result is not clear. A high degree of polarisation for any Raman line is generally accompanied by relatively large intensity but the converse relation is not true. Existing explanations for the polarisation phenomena in Raman spectra are briefly reviewed.

1. *Introduction.*

It has been pointed out by Sir C. V. Raman, in his first report of the discovery[1] that some of the modified lines

[1] Ind. Jour. Phys., Vol. 2, p. 387 (1928).

appearing in the scattered spectra are strongly polarised. In subsequent papers[2] the principal features regarding their state of polarisation have also been indicated. It need not be emphasised here that a more detailed and systematic study of their polarisation characters is a matter of great importance from a theoretical point of view. The question of intensity of the various Raman lines, the mutual relationship of the classical and the quantum scattering, the mechanism of the new phenomenon and various other fundamental problems are intimately related to that of polarisation. The subject has in the past received attention from Pringsheim, Cabannes, Daure and others. The close similarity that is usually observed between the Raman spectra of compounds having related structures is a fact of great significance recently brought out in a most striking manner in the cases of the various trichlorides and the tetrachlorides.[3] It is obviously of great interest to pursue such studies in various groups marked by simplicity of structure and extend them to other characters, in particular those of intensity and polarisation. Such results have been reported, especially by Cabannes,[4] but the information available is very meagre and hence the author has made a systematic study of the polarisation characters of the different Raman lines in the above series of trichlorides and tetrachlorides and in various other simple compounds, *viz.*, SO_2, SO_3, CS_2, $CHCl_3$, $CHBr_3$ and NH_3. The present paper consists of a description of the above results with a brief discussion of the same.

2. *Experimental.*

A large two prism glass spectrograph of high light gathering power made by Adam Hilger is made use of in the investigation. The light of a mercury lamp is focussed by a

[2] Proc. Roy. Soc., Vol. 122, p. 23 (1929).
[3] P. Daure, Compt. Rend., Vol. 187, p. 940 (1928).
[4] Mol. Spectra and Mol. Structure, Faraday Society Report, p. 813 (1929).

powerful condenser to the centre of the liquid under investigation contained in a suitable vessel, so arranged that the slit of the spectrograph is situated just far enough from it to allow the interposition of a large nicol. No lens is used for recondensing the scattered light on to the slit of the spectrograph. In most cases, the liquids purchased in the market have been purified by distillation in evacuated double bulbs. In some cases however, they have been used as such for convenience. Sulphur dioxide and ammonia are studied at the room temperature the liquids being preserved under pressure in sealed tubes.

Two spectrograms are always taken side by side on the same negative, one with the vibration direction of the nicol parallel to the track of light in the liquid and the other perpendicular, the conditions of illumination being identical in both cases. A difficulty however arises in the evaluation of the polarisation values especially if the exposures in the two cases are also identical. It is known from Fresnel's equations that after transmission through the boundary of any medium, the component polarised in the plane of incidence loses more than the one polarised normal to the plane of incidence and hence it must be inferred that the ratio of the intensities of the two components in the scattered light, a measure of the depolarisation in our case, is no longer the same before and after transmission through the spectrograph. The magnitude of the effect depends on the number of surfaces involved and on the obliquity of incidence on each surface. In consequence of the latter fact a slight dependence on the wave length may also be expected. It is therefore essential to calibrate the instrument in the range under investigation and suitably compensate for the same in the photometric evaluation of the polarisation. The slit is illuminated strongly by the direct light of a mercury lamp and the state of polarisation of each line determined visually by using a double image prism and a nicol suitably mounted on a graduated circle. Independent

determination is also made by the photographic method, by interposing a nicol in front of the slit and exposing the two components side by side on the same plate. Both lead to practically identical results and it is found that all the principal mercury lines of the visible region, *viz.*, λ4046, 4358, 4916, 5460 and the yellow doublet, in an initially unpolarised state, on transmission through the instrument acquire however a polarisation of 40%, the vertical component being weakened more than the horizontal. The result is probably correct to within ±5% and the variations with wave length do not seem to be so prominent as to produce changes greater than this figure. A computation based on Fresnel's equations, taking into consideration the situation of the prisms, in the instrument leads to a value very near the experimentally observed one. In order therefore to get the true polarisation of the Raman lines, the vertical component is always exposed for a longer time than the horizontal, the ratio of the exposures being 5:3. A plate containing graded exposures of the mercury spectrum is made use of in the evaluation of the ratio of intensities. The values given are relatively less accurate in cases of either very feeble or very intense lines.

3. *Results.*

The numbers in the brackets accompanying each frequency represent their relative intensities. ρ gives the ratio of the weaker to the stronger component, which may be termed the depolarisation of the particular frequency. The substances studied will be dealt with in different groups according to their structures.

Sulphur dioxide and carbon disulphide.—These two typical compounds are chosen to represent a triatomic molecule of the type AX_2. The differences between their Raman spectra, both in the number of frequencies and their characters are connected with the fact that CS_2 is a linear model whereas

SO_2	Frequency	526(0d)	1146 (10s)	1340 (0d)
	ρ	0·33	0·25	0·5
CS_2	Frequency	–	655 (10)	802 (2)
	ρ	–	0·25	0·25

SO_2 is a bent one.[5] It will be seen in the first instance that of the three frequencies in SO_2 the principal line which is marked by its extreme sharpness and great intensity is the best polarised, the degree of polarisation being the same as that of either of the CS_2 frequencies. Whether such a similarity in the polarisation characters implies any corresponding similarity in the nature of the three oscillations is at present very obscure. It must however be remarked here that corresponding to 1146 of SO_2 (8.73μ), a broad and intense infra-red absorption band has been recorded by Coblentz for this gas whereas CS_2 and CO_2 show no absorption in the infra-red corresponding to their principal Raman frequencies, *viz.*, 655 and 1284 respectively. This presumably implies that in the latter the oscillations involve no change in the electric moment, whereas in the SO_2 the great intensity of the absorption band suggests a considerable asymmetry of the oscillation. This may merely be the result of a difference in the geometry of the models and may not involve any essential difference in the characters of the oscillations. The other two weaker lines in SO_2 are less polarised and to different extents, suggesting that they represent distinct modes of oscillation.

Sulphur trioxide :—

Frequency :	290	370	534	666	697	1068	1271	1403	1489.
ρ		1	0·8	1	0·2	0·2	0·31	0·17	2	1

[5] A case analogous to that of CS_2 is CO_2 in which frequencies 1264·5, 1285·1, 1387·7 and 1408·4 are observed in the gaseous state. See Dickinson, Dillon and Rasetti, Phys. Rev., Vol. 34, p. 582, (1929).

The case of sulphur trioxide affords an interesting example in that it contains at ordinary temperatures a certain proportion of polymerised molecules S_2O_6. Of the above frequencies 534, 1068 and 1403 are due to SO_3 and the others to S_2O_6. Here again the principal line at 1068 is well polarised whereas the one of frequency 534 is perfectly unpolarised. The third broad line at 1403 constitutes an anomaly in that the depolarisation is distinctly greater than unity. In fact in the polarisation picture of SO_3, reproduced in a previous paper by the author, this line is to be seen distinctly in the spectrogram taken with the vibration direction of the nicol horizontal whereas it is hardly visible in the one taken with the vibration direction vertical. A similar result has been noticed by Cabannes[6] in certain crystals, especially calcite, but this is the first instance of a liquid showing a Raman line with a depolarisation greater than unity. The Raman line corresponding to this frequency and excited by the mercury line λ4046 shows however a different degree of polarisation, a result which is at the first sight very surprising. It so happens however that the antistokes component of an intense frequency 370 of S_2O_6 excited by λ4358 falls on this line and the apparent polarisation is evidently the resultant effect.

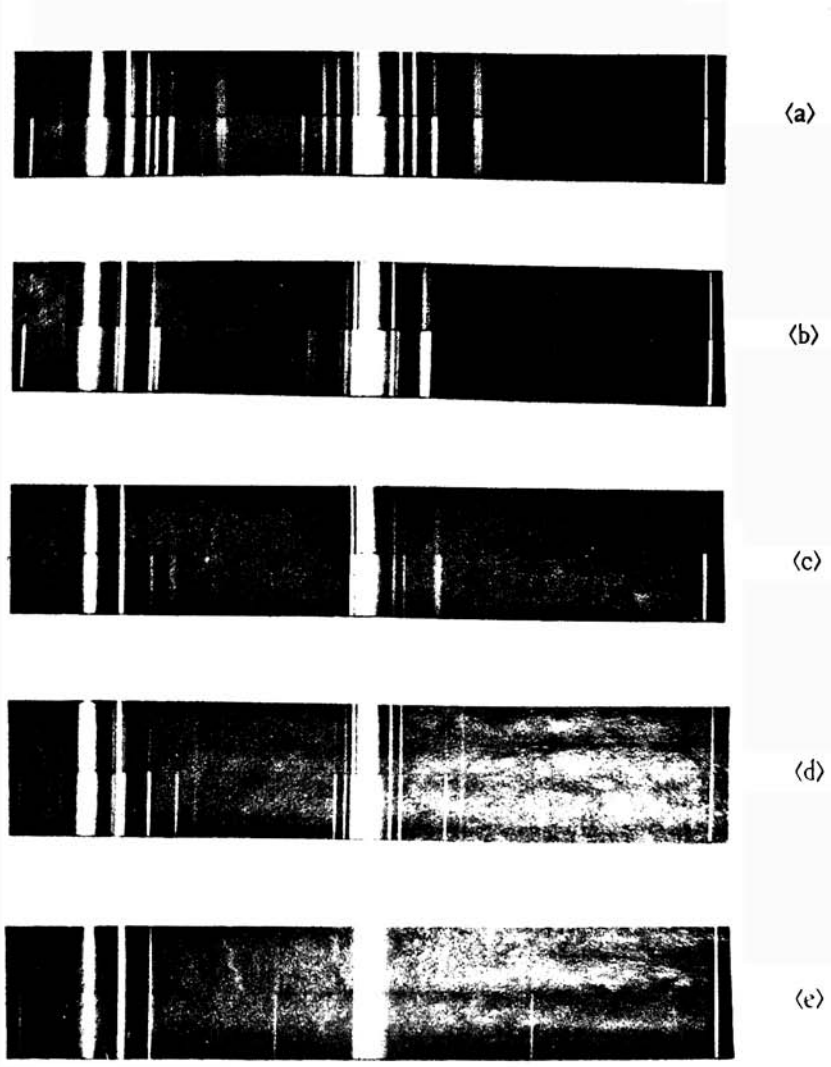
The Raman line corresponding to the largest frequency 1489 due to S_2O_6 shows an interesting structure in that it consists of a relatively bright and sharp central line with diffuse wings on either side. The central line is polarised to an appreciable extent whereas the accompanying wings are almost unpolarised. This no doubt suggests that the structure has a rotational origin but it is difficult to understand why it is prominent when associated with this frequency alone.

Ammonia :—

Frequency :	1070(od)	3216(2)	3304(4)	3380(1)
ρ	0·5	0·13	0·13	1

[6] Cabannes, *loc. cit.*

Polarisation of Raman Spectra.



(a) Carbon tetrachloride ; (b) Arsenic trichloride ;
(c) Phosphorus trichloride ; (d) Bromoform ; (e) Sulphur dioxide

In the polarisation picture of ammonia, reproduced in plate IV, it will be seen that of the group of four modified lines lying between λ4358 and 4916 lines of the mercury arc, the third is a broad and diffuse one presenting the appearance of a very imperfect polarisation. This is evidently due to the fact that two frequencies, *viz.*, 3216 excited by 4077 and 3380 excited by 4046 fall very near each other and give a superposed effect. The fact that 3380 is so imperfectly polarised contrary to the high degree of polarisation associated with 3216 is of great significance as it excludes the possibility of the components being due to a secondary Raman effect from the principal line 3304.[7]

Chloroform and bromoform:—

$CHCl_3$	Frequency :	263 (3)	366 (5)	668 (5)	768 (1d)	1222 (0)	1445 (0)	3025 (3)
	ρ	0·73	0·22	0·13	0.5	0·5	...	0·22
$CHBr_3$	Frequency :	154 (6)	222 (8)	538 (8)	654 (5b)	1146 (2)	1437 (0)	3023 (4)
	ρ	0·78	0·22	0·13	0·5	0·5	...	0·22

The line corresponding to a shift of about 1440 is so feeble in both cases that the polarisation could not be estimated with any certainty. The remarkable agreement between the spectra, their intensity relationships and their polarisation characters almost in every detail is too good a coincidence to be accidental, and is probably the strongest evidence in support of the view that they are all characteristic oscillations of the molecular model represented by CHX_3. The nature of X, its mass in particular, has very little influence on the general character of the radiations but as may be expected it loads the vibrating system resulting in a general diminution of the frequencies. It may be noted here that the third frequency given by 668 in chloroform and 538 in bromoform, is one of the most prominent ones and is the best polarised in both cases. The result is significant in that it suggests a resemblance to the AX_3 type, especially

[7] See J. B. Austin, Nature, Vol. 125, p. 464 (1930).

when the central atom is relatively lighter as in ammonia. This is intelligible if we regard the C-H group as replaced at its centre of gravity by a hypothetical atom of weight 13.

Trichlorides :—

PCl_3			$AsCl_3$			$BiCl_3$		
ν	I	ρ	ν	I	ρ	ν	I	ρ
190	10	0·88	159	8	0·86	96	8b	0·5
260	10	0·32	193	6	0·33			
488	2	0·75	370	6b	0·80	242	2b	0·75
512	10	0·14	410	10	0·17	288	10b	0·13

In the trichlorides of phosphorous and arsenic, it will be seen that the smallest frequency is very imperfectly polarised and the next in order comes the third which is however polarised to a small extent in both cases. The second one is fairly well polarised whereas the fourth is almost completely polarised (over 80%). In bismuth, the same general characters hold good except that the first broad band shows a value intermediate between those of the first and the second in the former cases, a result which obviously arises out of a superposed unresolved structure. The general similarity is again thus manifested very clearly in this series, the fluctuations from compound to compound in the actual values of the polarisation of any particular oscillation being surprisingly small especially if we remember that they constitute a very much larger range of variation in the masses of the vibrating parts than in $CHCl_3$ and $CHBr_3$ (P—31 to Bi—209).

Tetrachlorides:—

CCl_4			$SiCl_4$			$TiCl_4$			$SnCl_4$		
ν	I	ρ	ν	I	ρ	ν	I	ρ	ν	I	ρ
217	8	0·75	150	5	1	120	4	·8	106	5	1
313	8	0·8	221	5	0·9	145	0	0·83	131	6	1
459	10	0·1	426	10s	0·14	382	6	0·14	367	10	0·38
762	6	0·75	614	1d	1	494	0	0·5	403	6	0·8
792	6	0·75									
1537	2d	0·33	...	...	...	...	...	...	...	...	...

The polarisation characters of this series again show a strong resemblance between themselves as we pass from compound to compound. Ignoring the long shift of 1537 in CCl_4 we see that there are four frequencies in each case grouped into doublets, which are rather close in some cases. The general appearance of the spectrum thus resembles that of a trichloride. Contrary to this however, in these cases the third of the four Raman lines is the most prominent and the best polarised. The variation of both intensity and polarisation values for the different frequencies as we pass through the series is no doubt a little more marked here than in the case of either chloroform and bromoform or the trichlorides. The large discrepancy in the polarisation value given for 494 of $TiCl_4$ may partly be due to the extreme feebleness of the line. The case of CCl_4 however is slightly different from others in that the frequencies 217, 313 and the doublet at 770 show an appreciable amount of polarisation, whereas the corresponding frequencies in other cases are almost unpolarised. It is difficult to say if this is in any way connected with a probable anisotropic behaviour of the carbon atom itself.

The doublet at frequencies 762 and 792 is interpreted by

the author as a single initially degenerate frequency which has split up into two components owing to a slight departure of the molecule from a tetrahedral symmetry. Such a common origin is supported by the fact that their polarisation characters are very similar. The significance of an extra line at 1537 is difficult to understand and its extreme feebleness no doubt suggests that it is a harmonic of the doublet at 770. The line, although diffuse, presents no doublet appearance and the different extent to which it is polarised is hard to reconcile with the view that it is a harmonic.

It may finally be remarked that the polarisation of the principal line shows a marked imperfection as we pass from carbon, the lightest, to tin the heaviest of the central atoms. Contrary to this however, Daure[8] finds the principal line in the tetrachloride of tin to be as completely polarised as in that of carbon. In view of this the author has obtained two independent photographs with this substance in both of which this line shows a considerable amount of depolarisation.

4. *Discussion of the Results.*

The following general characters may now be described. The polarisation of all the Raman lines shifted by any particular frequency from the different exciting lines is the same. When however two different frequencies excited by different mercury lines happen to overlap, then an average value is obtained.

The stokes and antistokes components are polarised to the same extent.

The depolarisation—ratio of the weaker to the stronger component—of the several Raman lines varies very widely ranging from 0 to 1.

[8] Compt. Rend, Vol. 187, p. 940 (1928).

There is however one case, $\Delta\nu 1403$ in SO_3, whose depolarisation is greater than unity.

The general polarisation characters of the Raman spectra are very similar in compounds having analogous structures.

A high degree of polarisation is usually accompanied by a relatively large intensity although on the contrary it must be remembered that there are intense lines which are very imperfectly polarised.

The non-coherent nature of the Raman radiation[9] enables us to treat the problem of polarisation in a manner similar to the one adopted for the polarisation of Rayleigh scattering in gases, a state in which the mutual interference is so small that for all practical purposes the molecules act as independent sources of secondary radiation. The original explanation offered by Prof. Raman is based on the hypothesis that for a given energy transition, the molecule may be considered to have three principal directions with each of which is associated a different characteristic probability coefficient. Thus so far as the excitation of the molecule to a higher energy level is concerned it behaves as if it were an anistropic body, the degree of anistropy being different for different energy transitions. The coefficients of probability introduced here are in every respect analogous to the principal refractivities of the molecule in the theory of classical scattering and the above assumptions lead to an inherent depolarisation of every Raman line, the values ranging from 0 to $\frac{1}{2}$, the former representing the case, where the energy transition can take place with equal probability for all orientations of the molecule whereas the latter result is associated with a linear oscillator.

Of the subsequent attempts to give a satisfactory explanation of the phenomenon of polarisation, that of Cabannes may be mentioned here. From the theory of optical beats he has deduced a simple formula for a diatomic molecule

[9] See papers by Bogros, Rocard and others on the subject.

involving the depolarisation of the classically scattered light. This leads to a depolarisation of about 10% and 4·5% for the Raman radiation in the cases of hydrogen and oxygen respectively. The range of variation is between 0 and $\frac{6}{7}$.

Menzies attributed the two phenomena of complete polarisation and complete depolarisation to the cases where the direction of initial vibration is parallel and perpendicular respectively to that of the final vibration, intermediate inclinations giving rise to partial polarisation. This however presumes that two different vibrational energy levels are involved in the production of the Raman line. On the other hand in the quantum mechanical interpretation given by Hill and Kemble the polarisation of any Raman line is estimated by studying the relative magnitudes of the corresponding matrix elements associated with the three principal co-ordinate directions. A rough calculation made by them in the case of a diatomic molecule leads to a high degree of polarisation for Raman lines associated with vibrational transitions (about 80%). Besides the fact that the above theories lead us to such widely different conclusions a consideration of the actual experimental facts presents considerable difficulties in the way of a proper interpretation of this phenomenon. The tables will clearly show that there are values ranging from 0 to 1, and in one case the depolarisation is definitely greater than unity. The significance of the latter result is not at all clear.

Relation between intensity and polarisation.—As was remarked earlier, the well polarised lines are generally the intense ones—a result which will be more critically examined here. It is now known that for some reason, such oscillations as do not involve a change in the electric moment of the molecule come out with great intensity in the Raman spectra. The geometry of such oscillations, especially in the tetrahedral structures that are studied in this paper, is presumably represented by symmetric

expansions and contractions of the tetrahedra; the probability of the corresponding energy transition being also symmetric in that it is independent of the direction to a large extent. The latter fact involves a large polarisation of such symmetric oscillations and is in agreement with the observations. The conditions that govern the intensity of the Raman lines are however not constituted by the symmetry or otherwise of the oscillations alone, as cases of intense Raman lines with correspondingly prominent infra-red absorption maxima are well-known. Consequently an intense Raman line may or may not involve a high degree of polarisation.

In connection with polarisation, it may finally be remarked that the great similarity, exhibited by members belonging to a series represented by any particular molecule model, which persists through a large range of atomic weights is a strong evidence in support of the view that the geometry of the oscillation is one of the principal factors that govern the state of polarisation of the scattered light. A simple picture of the relation is rendered difficult by the fact that the oscillations in most of the above cases are already very complex. A study of the various diatomic molecules of widely varying masses is evidently of great utility in affording a crucial test of several of the above observations and is now being undertaken by the author.

In conclusion the author desires to express his best thanks to Prof. Sir C. V. Raman for his kind interest and encouragement in the work. All the problems described in the paper have been taken up at his suggestion.